

CO HYDROGENATION AND OXYGENATE FORMATION OVER RUTHENIUM SUPPORTED
ON A BASIC LAYERED DOUBLE HYDROXIDE

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ABSTRACT

Synthetic layered double hydroxides (LDH) such as hydrotalcite (HT), $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}](\text{CO}_3) \cdot 4 \text{H}_2\text{O}$, provide a highly basic ($\text{pK}_a < 35$) environment for supporting transition metals. Ruthenium was grafted onto a HT using $\text{Ru}_3(\text{CO})_{12}$ as a precursor and was subsequently reduced under flowing H_2 at 275°C to ruthenium metal. The supported catalyst exhibited substantial selectivity at 275°C for $\text{C}_1\text{-C}_4$ alcohols at moderately low pressures (0-190 psig). Methanol was the most dominant oxygenated product. The factors effecting the thermal stability and selectivity properties of this new class of catalyst system are presented.

INTRODUCTION

Layered double hydroxides, such as hydrotalcite $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}](\text{CO}_3) \cdot 4 \text{H}_2\text{O}$ (HT, 3:1 Mg:Al), are anionic clay minerals. These compounds have a brucite-like structure, with positively charged hydroxide layers of aluminum and magnesium. The positive charge is compensated by intercalated carbonate anions along with some water molecules. The thermal decomposition of this material has been investigated by several laboratories [1-3]. These earlier studies indicate that the interstitial water is reversibly lost up to 200°C . Between 250°C - 450°C , the loss of water was accompanied by dehydroxylation. Reichle [3] has reported that only above 275°C the formation of MgO phase along with HT phase was observed by X-ray diffraction (XRD). Beyond 550°C the HT phase was irreversibly lost.

Giannelis et al. [4] have grafted metal carbonyl complexes onto the pillars within the galleries of aluminum pillared montmorillonite (APM) clays. They reported that $\text{Ru}_3(\text{CO})_{12}$ is more easily transformed into partially oxidized grafted species, even in the absence of air, when compared with other carbonyl complexes. Giannelis and Pinnavaia [5] further extended their studies to include the grafting of Rh and Pt carbonyls to the surfaces of HT. In the present study we show that it is possible to graft these carbonyl complexes onto HT.

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Bulk Ru is known to be one of the most active syngas conversion catalyst with almost 100% selective to straight chain hydrocarbon [6,7]. However, the acid-base properties of the support are known to effect the selectivity of Group VIII transition metals. Thus, hydrotalcite provided us with an ideal opportunity to investigate the behavior of $\text{Ru}_3(\text{CO})_{12}$ and Ru on a very basic oxide surface.

EXPERIMENTAL

HYDROTALCITE PREPARATION

A solution of 51.2g (0.20 mols) $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 24.8g (0.067 mols) $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 200 ml of water was added drop wise to a solution of 25g (0.20 mols) $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ and 28g (0.70 mols) NaOH in 200 ml of water. The addition was stopped when the pH of the solution reached 10. This process, which took about 4h, was carried out with vigorous agitation. The resulting heavy slurry was refluxed at $65 \pm 5^\circ\text{C}$ for 16h with continuous mixing. Upon cooling, the slurry was washed and centrifuged several times until almost all the salt was recovered. The slurry was then dried in air on a large glass plate [8]. The X-ray pattern indicated a d_{001} spacing of 7.76Å, which is indicative of HT with 3:1 Mg:Al. The thermal stability of the HT thus prepared was analyzed using a CAHN TGA 121 thermo-gravimetric analyzer from 25 to 1000°C at a heating rate of $5^\circ\text{C}/\text{min}$. The weight loss under isothermal conditions at 275°C also was investigated. The isothermal temperature was achieved using the same heating rate indicated earlier.

RUTHENIUM IMPREGNATION

One gram of HT was evacuated at room temperature for 4h. To this HT was added to 45mg of $\text{Ru}_3(\text{CO})_{12}$ dissolved in 100 ml of degassed CH_2Cl_2 . The slurry was stirred for 20h, filtered in air, and washed with a small amount (~20 ml) of CH_2Cl_2 . The percentage of Ru impregnated was determined by atomic adsorption (Galbraith Laboratory) and was found to be 0.34%. A 3.0% mixture of Ru-HT catalyst and KBr was pelletized. The IR spectrum was recorded on an IBM Model IR/44 FTIR spectrometer.

CO-HYDROGENATION

About 0.5g of Ru-HT catalyst was loaded into a 1/4" OD, 316 stainless steel, tubular, single pass reactor. The catalyst sample was reduced in flowing hydrogen (Matheson, UHP) at 275°C for 6h. The reduction temperature was achieved at a heating rate of $5^\circ\text{C}/\text{min}$. The CO hydrogenation reaction was carried out between 225 - 275°C , and from atmospheric pressure to 190 psig at a conversion of less than 5%, in order to avoid mass and heat transfer limitations. A H_2/CO flow ratio of 2.0 was maintained

using mass flow controllers. The incoming gases were further purified by passing through a manganese/silica [9] oxygen scrubber, Linde 4Å molecular sieve to remove water and through an Al_2O_3 trap maintained at 200 K to remove metal carbonyls. The reactor effluent was transferred through a heated line to a Hewlett-Packard 5890A GC equipped with automatic gas sampling valve and flame ionization detector. The hydrocarbons were separated using a 60m-long, 0.25 mm dia, 1µm-thick SP2100™ coated, fused silica capillary column.

RESULTS AND DISCUSSIONS

The thermogram presented in Figure 1 for $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\cdot\text{CO}_3\cdot 4\text{H}_2\text{O}$ exhibits four distinct regions, in agreement with the observations of Reichle [3]. The first region (25°-250°C) was attributed to the loss of interstitial water. At the second region (250°-325°C) the loss of water is accompanied by slow dehydroxylation. In the third (325°-500°C), rapid dehydroxylation and loss of carbonate are accompanied by HT phase transformation to mixed metal oxides. In the final region (>500°C), a stable mixed-oxide phase is irreversibly formed. According to Reichle [3], the highest temperature at which the HT phase was stable is 275°C. Therefore, we investigated the thermal stability of HT at 275°C temperature for 4h. As seen in Figure 2, there was no loss in weight after reaching 275°C over 4h period. A similar thermal treatment at 350°C resulted in a significant loss of weight even at the isothermal condition. Therefore, we used 275°C as the reduction temperature for ruthenium and the highest reaction temperature for CO hydrogenation.

The FTIR spectrum for the $\text{Ru}_3(\text{CO})_{12}$ -HT impregnation product is presented in Figure 3. The two peaks at 2047 and 1965 cm^{-1} were assigned to a mononuclear $[\text{Ru}(\text{CO})_x(\text{OM})_2]_n$, grafted species [4,5,10]. In this case M is either Al or Mg ions. The degradation of the neutral metal cluster carbonyl, due to their reaction with surface hydroxyl groups, results in the formation of partially oxidized grafted species on the surface of HT. Analogous species osmium complex were known to form on bulk silica and alumina supports [11-13].

The selectivity of the hydrogen-reduced Ru-HT catalyst for various hydrocarbon at 275°C at pressures ranging from 0-190 psig is tabulated in Table 1. The production of methane decreased while the total alcohol synthesis increased with increasing pressure. An opposite trend was observed with increasing temperature (Table 2). That is, the methane production increased while the alcohol production decreased when the temperature was raised from 260 to 275°C at a constant pressures of 120 psig. The percentage of various alcohols produced are presented in Table 3 as a function of pressure at 275°C. In Table 4 the selectivity is presented as a function of temperature at a constant pressure of 120 psig. It is interesting to note that

the methanol fraction is independent of pressure, but it increases with increasing temperature at constant pressure.

Metals such as Pt, Pd and Ir are known to non-dissociatively adsorb CO even at high temperature and to produce methanol almost exclusively [14]. Katzer et al [14] observed that the methanol production was related to the concentration of non-dissociatively adsorbed CO. Rhodium, however, is selective to both alcohols and hydrocarbons, depending on the nature of the material that supports it [15-17]. Rh supported on MgO is more selective towards MeOH, but when supported on a non-basic material, it is selective to hydrocarbons.

Ruthenium is known to dissociate CO at reaction temperatures and to produce mainly hydrocarbons. There are a few exceptions, of course. Some workers [18,19] have reported about 20% selectivity to alcohols for alkali promoted Ru and for Ru on MgO catalysts at pressure of 300-1000 psig. It appears that the basic environment of the Ru is responsible for such high selectivity for alcohols. The selectivity toward alcohols for the Ru-HT observed in this study is comparable to that for Ru on MgO or alkali-promoted Ru catalysts [18,19]. It is particularly noteworthy, however, that the reaction pressure employed in this study was far less than the others.

Since HT is an extremely basic material, it appears that it has altered the characteristics of Ru metal by limiting the dissociation of CO. The lower methane production and higher alcohol yield (in particular, the higher MeOH yield) at lower temperature supports this hypothesis. At higher temperatures, the CO disassociation is increased and thus the methanation reaction is promoted; at the same time, the lower concentration of undissociated CO reduces the selectivity of alcohols.

SUMMARY

Our results clearly demonstrate that the support material can alter the CO hydrogenation selectivity of ruthenium. This metal typically is highly selective to straight-chain hydrocarbons, but the selectivity at relatively low reaction pressures has been altered by the presence of a basic support to produce alcohols. In fact, the alcohol selectivities reported here for Ru have not been achieved at such low pressures previously.

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Table 1

CO Hydrogenation Selectivity of Ru/HT at Various Pressures
(275°C)^a

Pressure (psig)	Hydrocarbon and Total Alcohol Yields, Wt %							
	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇₊	ALC
0	85.5	8.8	5.7	tr				0.0
70	65.2	8.3	7.0	4.5	2.8	1.0	0.9	10.0
120	63.5	7.5	7.4	4.5	2.4	1.1	0.4	13.2
170	54.1	7.6	9.1	6.0	3.3	1.5	1.0	17.6
190	56.7	8.0	9.7	6.1	3.5	2.4	0.7	21.8

^aH₂/CO = 2, Conv<5%, GHSV = 1000 to 3000 h⁻¹, ~ 0.5g of catalyst.
Time on stream >24h.

Table 2

CO Hydrogenation Selectivity of Ru/HT at Constant Pressure
(120 psig)^a

Temp. (°C)	Hydrocarbon and Total Alcohol Yields, Wt %							
	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇₊	ALC
260	48.0	7.0	9.3	6.7	4.0	3.5	tr	20.8
275	63.5	7.5	7.4	4.5	2.4	1.1	0.4	13.2

^aH₂/CO = 2, Conv<5%, GHSV = 1000 to 3000 h⁻¹, ~ 0.5g of catalyst.
Time on stream >24h.

Table 3

C₁-C₄ Alcohol Distribution in the Total Alcohol Product Stream
for Ru/HT at 275°C^a

Pressure (psig)	MeOH	EtOH	PrOH	BuOH
0	0	0	0	0
70	78	22	0	0
120	75	20	5	0
170	78	18	4	0
190	74	17	4	4

$\bar{a}_{H_2/CO} = 2$, Conv<5%, GHSV = 1000 to 3000 h⁻¹, ~ 0.5g of catalyst.
Time on stream >24h.

Table 4

C₁-C₃ Alcohol Distribution in the Total Alcohol Product Stream
for Ru/HT at 120 psig^a

Temperature (°C)	MeOH	EtOH	PrOH
260	81	13	6
275	75	18	4

$\bar{a}_{H_2/CO} = 2$, Conv<5%, GHSV = 1000 to 3000 h⁻¹, ~ 0.5g of catalyst.
Time on stream >24h.

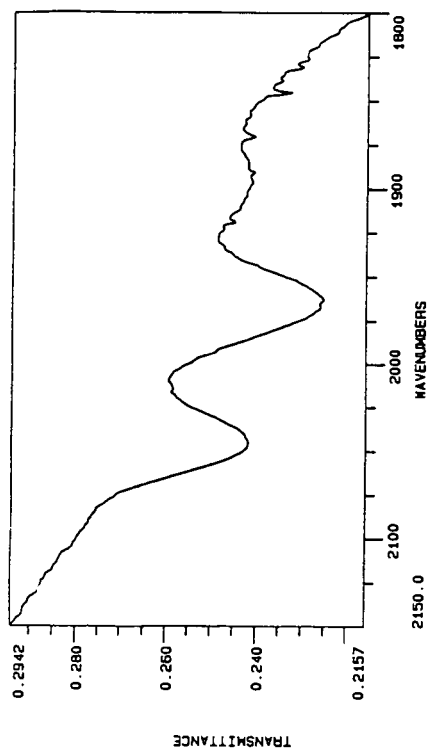


Figure 1 FTIR spectrum of the reaction product obtained from the "impregnation" of $\text{Ru}_3(\text{CO})_{12}$ on HT. The two major peaks at 2047 and 1965 cm^{-1} indicate the presence of grafted $\text{Ru}(\text{CO})_x(\text{OH})_n$.

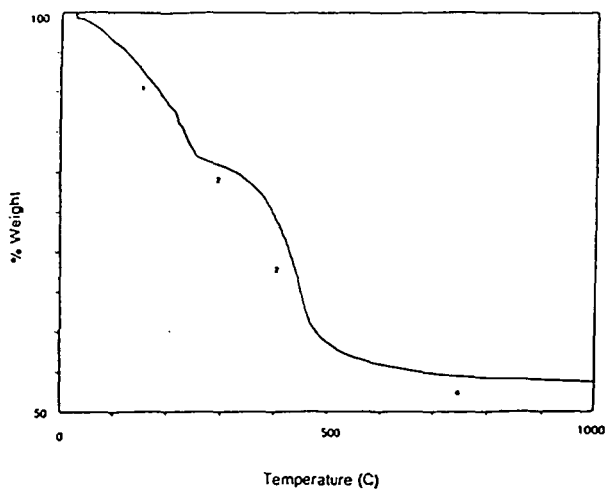


Figure 2 Thermogravimetric analysis of HT. The heating rate was $5^{\circ}\text{C}/\text{min}$. The four (1-4) regions are discussed in the text

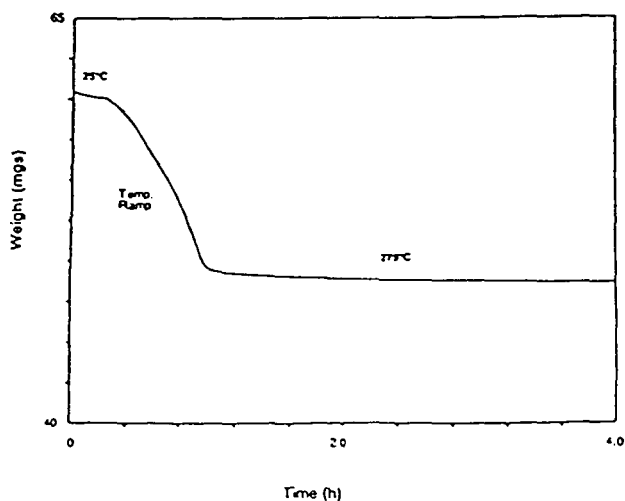


Figure 3. Thermogram of HT. Heating from 25° to 275°C was achieved using a temperature ramp of $5^{\circ}\text{C}/\text{min}$.